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Use of wood elemental composition to predict heat treatment intensity and decay resistance of different softwood and hardwood species

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ABSTRACT

Heat treatment is an attractive alternative to improve decay resistance of low natural durability wood species. Decay resistance is strongly correlated to thermal degradations of wood cell wall components. Some recent studies proposed the use of wood elemental composition as a valuable marker to predict final properties of the material. These results, initially obtained with pine, have been extended to different softwood and hardwood species to check validity of the method using equipment specially designed to measure mass losses during thermal treatment. Heat treatment was performed on two softwood species (pine and silver fir) and three hardwood species (poplar, beech and ash) at 230 °C under nitrogen for different times to reach mass losses of 5, 10 and 15%. Heat-treated specimens were exposed to fungal decay using the brown rot fungus *Poria placenta* and the weight losses due to fungal degradation determined as well as initial wood elemental composition. Correlations between weight losses recorded after fungal exposure and elemental composition indicated that carbon content and O/C ratio can be used to predict wood durability conferred by heat treatment. Moreover, it was observed that for given curing conditions thermo-degradation patterns differed considerably according to the wood species. The sole analysis of wood physical properties like its density, thermal conductivity and diffusivity cannot allow explaining the observed differences, which should also depend on thermally activated chemical processes depending on wood chemical composition.

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1. Introduction

The use of wood as building material is subject to increasing interest due to its intrinsic properties and its ability to fix carbon dioxide. Wood heat treatment by mild pyrolysis has been reported to improve some of its properties such as its biological durability and its dimensional stability. This process avoids the use of wood preservatives, constituting an attractive "non biocidal" alternative to classical preservation treatments. Indeed, even if heat treatment generates some volatile organic compounds and waste water having strong acidic and corrosive effect, it remains globally relatively safe for the environment. The influence of treatment conditions on chemical composition and conferred properties of heat-treated wood have therefore been intensively studied. Wood heat treatment induces chemical modifications of the main wood cell wall components. The lignin network is modified [1–5], the ratio between amorphous and crystalline cellulose is also changed [6–8], hemicelluloses are strongly degraded [7,9] leading to formation of carbonaceous material within the wood [10]. These chemical modifications modify wood colour [11–13] and confer to the material new properties such as improved dimensional stability [14,15], improved fungal resistance [16–18], lower affinity for water due to increase of wood surface hydrophobicity [18–22]. Different heat treatment conditions have been described in the literature [23,24]. Among these, the wood torrefaction corresponds to heat treatment carried out at temperatures below 300 °C under inert gaseous atmospheres. Chemical reactions involved during torrefaction as well as final properties of the material depend strongly on the treatment temperature and of its duration. During torrefaction, wood is thermally decomposed at a slow rate [25]. Recently, it was reported that the anhydrous mass loss during the heat treatment could be a reliable and accurate marker to predict decay resistance of heat-treated wood [17,26]. Hence, the control of the mass of the material during the heat treatment process will allow predicting its final durability. Due to the importance of dehydration reactions occurring during the heat treatment, the behaviour of carbon and oxygen contents has been evaluated through determination of wood's elemental composition [27] and reactivity of free hydroxyl groups with acetic anhydride [4]. Indeed, previous studies have shown that heat treatment resulted in numerous dehydration

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reactions due to degradation of amorphous polysaccharides [6–8] jointly with the formation of carbonaceous materials within the wood structure leading to a strong decrease of wood's O/C ratio [3,10]. Moreover, dehydration reactions occurring during heat treatment have been reported to be at the origin of the lower reactivity of hydroxyl groups of wood cell wall polymers during acetylation [2,4]. The purpose of this study is to evaluate the correlations between the improvement of the durability of different softwood and hardwood species and the mass losses induced by the heat treatment estimated on the basis of their O/C ratio.

2. Materials and methods

2.1. Materials

Samples were cut from heartwood boards of different softwood and hardwood species: beech, *Fagus sylvatica* L.; poplar, *Populus nigra*; ash, *Fraxinus excelsior* L.; pine, *Pinus sylvestris* and Silver fir, *Abies pectinata*.

2.2. Heat treatment

Heat treatment was performed under nitrogen on the different species by conduction between two metallic heating plates placed on a precision balance allowing recording of dynamic mass loss as a function of time and temperature (Fig. 1). Dimension of the boards used for heat treatment was $2.5 \times 11 \times 25\ \mathrm{cm}^3$ (R, T, L). Wood specimens were oven dried at 103 °C during 48 h prior to heat treatment. Weight of the sample was recorded automatically all along the experiment and mass loss due thermo-degradation calculated according to the formula:

$$\mathrm{ML}\ (\%) = 100 \times (m_0 - m_1)/m_0$$

where m_0 is the initial oven dried mass of the sample before heat treatment and m_1 the oven dried mass of the same sample after heat treatment.

2.3. Microanalysis

Wood was grounded to fine sawdust and passed through different sieves to obtain a powder of granulometry comprised between 0.2 and 0.5 mm. Sawdust was conditioned at 103 °C for 24 h. and stored in closed bottle before analysis. Elemental analyses were performed on a Thermofinnigam Flash EA1112 micro-analyser.

2.4. Fungal durability

Wood blocks of $5 \times 10 \times 30\ \mathrm{mm}^3$ were cut from heat-treated boards for fungal durability evaluations. Petri dishes (9 cm diameter) were filled with sterile medium (20 mL) prepared from malt (40 g) and agar (20 g) in distilled water (1 L) and inoculated with a piece of mycelium of a freshly grown *Poria placenta* culture. Petri dishes were incubated at 22 °C and 70% HR until full colonization of the surface's medium by the mycelium. Two heat-treated specimens and one untreated sample were placed in each Petri dishes and exposed to the brown rot fungus for 16 weeks. Each experiment was duplicated. At the end of test period, mycelia were removed and the blocks were dried at 103 °C and weighed (m_2) to determine the weight loss caused by the fungal decay:

$$\mathrm{WL}\ (\%) = 100 \times (m_{0\ \mathrm{or}\ 1} - m_2)/m_{0\ \mathrm{or}\ 1}$$

where $m_{0\ \mathrm{or}\ 1}$ are respectively the initial oven dried mass of untreated or heat-treated wood blocks before fungal exposure and m_2 is the oven dried mass after fungal attack.

3. Results and discussion

Mass losses of the different wood species as a function of time are presented in Fig. 2 for similar curing conditions. Mass loss depends of the density but also of the nature of the wood species. Until 160 °C, only very small mass losses were observed corresponding to vaporization of volatile extractives and of bound water absorbed on the wood fibres. Thermo-degradations begin at higher temperatures and are effective at 230 °C. Species of lower density present better stability to thermo-degradation than species of higher density. A first attempt to explain this difference is associated to intrinsic thermal properties of each wood species. Indeed, the phase of heat transfer may differ according to thermal properties of each species limiting thermo-degradation reactions. Diffusivity α ($\mathrm{m}^2\ \mathrm{s}^{-1}$) is calculated from the following relation:

$$\alpha = \lambda/\rho \cdot C_\mathrm{P}$$

where λ is the conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$) given by literature, ρ the density ($\mathrm{kg\,m^{-3}}$) measured for each wood species, and C_P the specific heat, which depend on the temperature according to the formula:

$$C_\mathrm{P} = 1112 + 4.85(T - 273)$$

where T is the temperature in K.

Due to the transient mode during heat treatment, it is difficult to determine diffusivity with precision. Indeed, all parameters vary with time and temperature as the thermo-degradation reactions take place, so that it was difficult to evaluate diffusivity. For these reasons, diffusivities were calculated for each wood species at the beginning and at the end of the treatment.

Data are given in Table 1. Beech and ash, which present the higher densities and conductivities and lower diffusivities are degraded more rapidly, while pine, fir and poplar which present the lower densities and conductivities and higher diffusivities are less

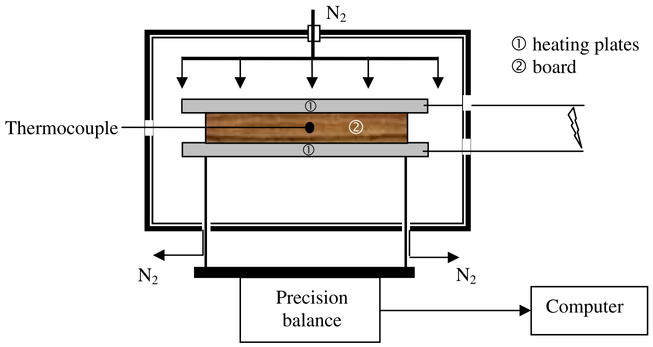

Fig. 1. Schematic equipment used for heat treatment.

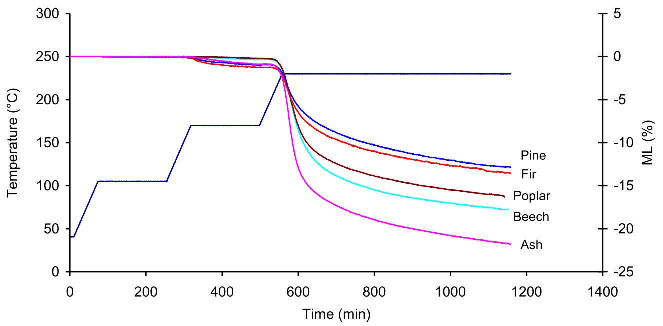

Fig. 2. Evolution of mass during heat treatment of different wood species.

Table 1
Thermal properties of the different wood species before and after thermal treatment at 230 °C.

Species	Density ($kg\,m^{-3}$)		Conductivity ($W\,m^{-1}\,K^{-1}$)		Diffusivity ($m^2\,s^{-1}$)	
	Before	After	Before	After	Before	After
Beech	653	591	0.1544	0.1420	1.06×10^{-7}	1.08×10^{-7}
Poplar	437	394	0.1112	0.1026	1.14×10^{-7}	1.17×10^{-7}
Ash	675	589	0.1588	0.1416	1.06×10^{-7}	1.08×10^{-7}
Pine	461	439	0.1160	0.1116	1.13×10^{-7}	1.14×10^{-7}
Fir	447	410	0.1132	0.1058	1.14×10^{-7}	1.16×10^{-7}

susceptible to thermo-degradation. However, other parameters should be involved to explain the differences observed between the two softwoods species and poplar, which present quite similar thermal properties but different thermo-degradation patterns. Softwoods and hardwoods differ in the percentage and the composition of hemicelluloses. Softwoods contain galactoglucomannan and arabinoglucuronoxylan, while hardwoods contain mainly glucuronoxylan and low amount of glucomannan. Moreover, xylan units of hardwood glucuronoxylan are strongly acetylated, comparatively to softwood hemicelluloses for which acetyl groups are attached to the glucomannan backbone [6,28]. Deacetylation of hemicelluloses causes liberation of acetic acid, which catalyses depolymerisation of the less ordered carbohydrates like hemicelluloses and amorphous cellulose. Higher content of acetyl groups present in hardwoods may be at the origin of the higher kinetic of thermo-degradation observed for poplar comparatively to softwoods species. Similarly, differences in chemical composition should be involved to explain differences of thermo-degradation patterns observed for beech and ash, which present quite similar densities and diffusivities.

Starting from thermo-degradation curves, it was possible to estimate curing times to reach a given mass loss. Each wood species was heat treated during different times to reach mass losses of approximately 5, 10 and 15%. Elemental composition and durability against the brown rot fungus *P. placenta* were then measured. Correlations between mass losses and carbon content, O/C ratio as well as fungal durability are presented in Figs. 3–5. As expected, wood carbon content increases as the mass loss increases, while oxygen content decreases [27,29]. For a similar mass loss, softwoods present higher carbon content than hardwoods. In all cases, evolution of carbon content increases linearly as the mass loss increases showing a good correlation between mass loss and carbon content. Even if the kinetics of thermo-degradation are different, their effects on wood chemical composition for a same level of degradation are relatively close. This is not surprising considering that the main modifications occurring during wood heat treatment are due to degradation of hemicelluloses through depolymerisation reactions to C5 and C6 monosaccharides leading after dehydration to furfural, hydroxymethylfurfural or levoglucosenone (Fig. 6). These products may either be loss by evaporation or subject to further degradation leading to furan, formaldehyde, formic acid, levulinic acid and other by-products involved in thermo-condensation or thermo-reticulation with lignin [1,10,30,31]. From a chemical point of view, it seems reasonable to think that quite similar products were formed for a similar mass loss making abstraction of the initial chemical differences existing between softwoods and hardwoods. The main difference concerns the kinetic of thermo-degradation, which differs significantly between softwoods and hardwoods. This difference may be explained by the higher acetyl content present in hardwoods leading to the formation of higher quantities of acetic acid involved in acidic catalysis of hydrolysis and dehydration reactions, but also by the higher susceptibility to hydrolysis of pentoses present in hardwoods hemicelluloses [32]. Correlations between mass loss and atomic O/C ratio are shown in Fig. 4. O/C ratio decreases linearly with the increase of the mass loss indicating that O/C ratio could be a valuable marker of heat treatment intensity. This decrease can be mainly attributed to thermal degradation of wood mentioned above and subsequent dehydration reactions explaining the decrease of oxygen content. Even if each wood species presents different behaviour, the tendencies observed remained the same indicating formation of degradation products with relatively similar structures. Except for untreated fir, higher atomic O/C ratios were obtained with hardwoods. This observation can be explained by the higher syringyl content of hardwoods lignins compared to softwoods, which contain mainly guaiacyl units. Similarly to our previous results obtained with pine, the strong correlations observed between mass losses due to thermal degradations and O/C ratios allow

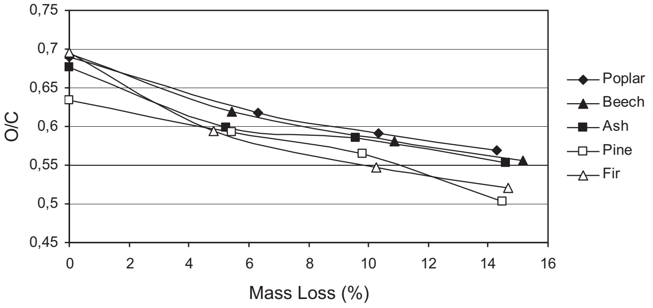

Fig. 4. Correlation between mass loss resulting from heat treatment at 230 °C and O/C ratio for different wood species.

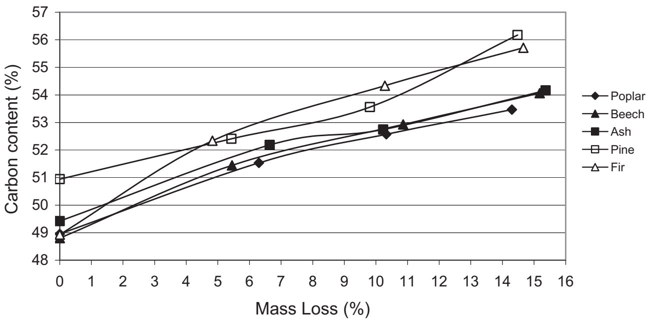

Fig. 3. Correlation between mass loss resulting from heat treatment at 230 °C and carbon content for different wood species.

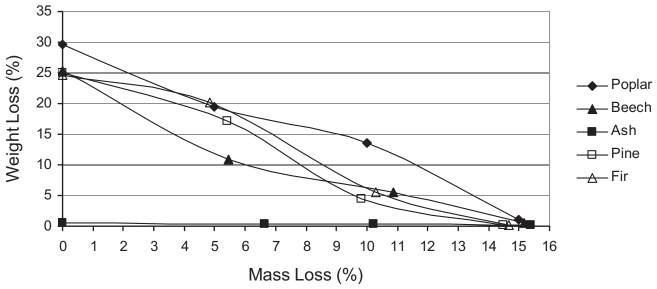

Fig. 5. Correlation between mass loss resulting from heat treatment at 230 °C and weight loss due to fungal degradation for different wood species.

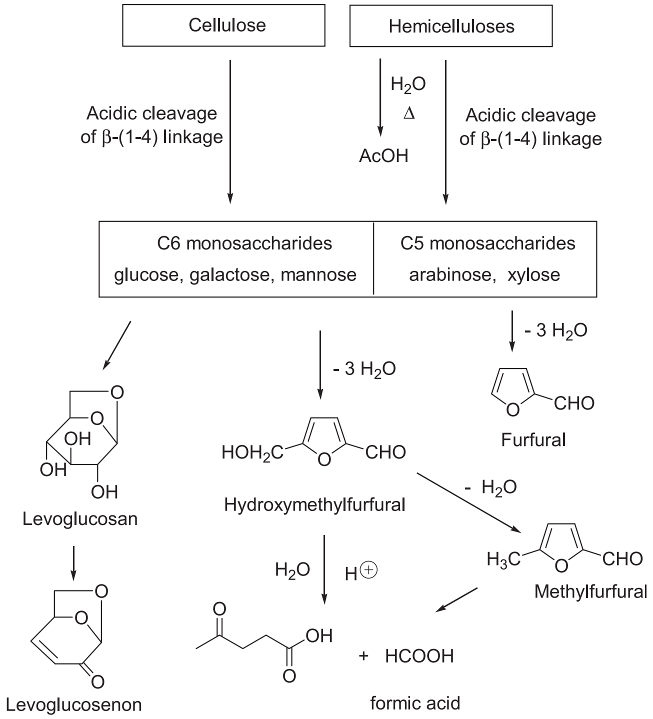

Fig. 6. Depolymerisation and degradation products of polysaccharides.

envisaging O/C ratio or carbon content as valuable markers of the heat treatment intensity.

Correlation between mass loss due to heat treatment and weight loss due to fungal degradation are shown in Fig. 5. In a way similar to what is practised on industrial scale, we have chosen to perform heat treatment on the heartwood of the different wood species studied. Indeed, all these species are characterized by a relatively low natural durability and are therefore particularly suitable for heat treatment. Except in the case of ash, which was totally resistant to biodegradation in the tested conditions, all wood species present weight losses in direct connection with their degree of thermo-degradation. Similarly to our previous results obtained with pine, conferred durability increase with treatment intensity. Independently of the wood species used, wood samples become totally resistant to decay for mass losses around 15%. This value can be associated to a carbon content of approximately 56% for softwoods and 54% for hardwoods, confirming the possibility to use wood elemental composition as a marker to predict decay durability of heat-treated wood.

4. Conclusion

The results of this study highlighted that there is no simple relation between the wood's thermal characteristic and the thermal degradation rate. Even if wood species of lower densities seems to be more resistant to thermal degradation, other parameters should be also involved to explain differences in thermal degradation patterns observed between softwood and hardwood species of similar densities or hardwoods species of similar densities. The kinetics of the mass loss during the heat treatment is strongly dependent on the wood composition and especially its content of acetyl groups. The study has also shown a good correlation between the mass loss, the elemental composition and the fungal durability, confirming the possibility of predicting the decay durability of heat-treated woods on the basis of their carbon content or O/C ratio. Further studies are in progress to validate this method on industrially heat-treated samples in order to develop a quality control method aimed to certify the product quality to the customers.

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